

Carbon monoxide measurements from 76° N to 59° S and over the South Tasman Sea

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Abstract. In November and December of 1995, carbon monoxide (CO) measurements were made in a Pacific transect and over the South Tasman Sea as part of the First Aerosol Characterization Experiment (ACE 1) program. Airborne CO measurements were made from 76° N to 59° S. A clear latitudinal gradient in CO concentrations was measured, with the southern hemisphere average about 80 parts per billion by volume (ppbv), and increasing to 120–130 ppbv at the most northern latitudes. Plumes of CO with a 30–40 ppbv concentration increase over the general background concentrations could be seen at several latitudes. The National Oceanic and Atmospheric Administration R/V *Discoverer* made CO measurements over the South Tasman Sea from November 15 to December 9, 1995. A systematic decrease of 0.31 ppbv/d CO was observed. Vertical profile measurements of CO from near the ocean surface to 2500 m altitude during the Lagrangian B intensive of ACE 1 suggested the mixing of stratospheric air with reduced CO concentrations.

1. Introduction

There are a number of sources for atmospheric CO [Taylor *et al.*, 1996]. The two main ones are the photochemical oxidation of atmospheric hydrocarbons and emissions from the incomplete combustion of hydrocarbon fuels. Motor vehicles contribute about half the CO from fuel combustion, but the total amount emitted is decreasing as more regulations on vehicle emissions are imposed. Recent estimates of the atmospheric CO input ascribe 55% to photochemical hydrocarbon oxidation, 25% to incomplete hydrocarbon combustion, 15% to biomass burning, and the remainder to vegetation, oceanic, and soil sources [Taylor *et al.*, 1996].

There is a strong hemispheric gradient [Novelli *et al.*, 1992] and seasonal cycle in atmospheric CO concentrations [Brunke *et al.* 1990; Novelli *et al.*, 1992]. The CO source strength is stronger in the northern hemisphere (NH) than in the southern hemisphere (SH), and the atmospheric lifetime of a few months for CO is less than the hemispheric mixing time of a year, leading to higher concentrations in the NH. The seasonal variation is in excess of 100 ppbv at Barrow (71.32° N), between 40–60 ppbv at 20° N [Novelli *et al.*, 1992] and drops to 25 ppbv at 34.35° S [Brunke *et al.*, 1990]. The major loss mechanism for CO is reaction with OH radical, which drives the seasonal cycle, leading to a minimum concentration in late summer and a maximum in winter. The maximum/minimum in the CO concentration lags the solar minimum/maximum by approximately 2 months.

Currently, a majority of the atmospheric CO monitoring is conducted with a network of ground stations, and the samples

are sent back to a central laboratory for analysis [Novelli *et al.*, 1992]. A gas filter radiometer has been deployed on the space shuttle for several missions [Reichle *et al.*, 1986; 1990]. This instrument has the potential of mapping the atmospheric CO concentration from a single spaceborne platform.

In this paper, we report atmospheric CO measurements made during the southern hemisphere marine aerosol First Characterization Experiment (ACE 1) [Bates *et al.*, this issue]. In addition to providing an extensive CO data set covering much of the Pacific region, the CO data will be a crucial component in modeling the OH data for comparison with the airborne OH measurements conducted from the C-130. [Suhre *et al.*, this issue; Mauldin *et al.*, 1997]. These measurements were made from the research vessel *Discoverer* over the South Tasman Sea and from the National Center for Atmospheric Research (NCAR) C-130 aircraft.

2. Experimental

2.1. Measurement Region and Observational Approach

As part of the ACE 1 program, the ferry flights of the aircraft to the South Tasman Sea study region were also used for research. This provided measurements from 76°N to 59°S over the Pacific Ocean.

CO measurements in the primary ACE 1 study area, the South Tasman Sea, were made from both ship and aircraft. The ship measurements were from November 15 through December 9, 1995, and the aircraft measurements were from November 18 to December 12, 1995. The measurement region covered from 40°–55°S and 135°–160°E. Complete details on the *Discoverer* cruise tracks and the C-130 flight tracks are given by Bates *et al.* [this issue].

Seventy one of ACE 1 aircraft flight hours were used for two Lagrangian experiments [Bates *et al.*, this issue]. In these

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experiments, the goal was to track the chemical evolution of an air parcel for up to 48 hours. Constant-level balloons designed to advect with the winds (S.A. *Businger et al.*, unpublished manuscript, 1998) are used to mark the air parcel. The aircraft carried a radio receiver for the balloons, and after sampling in the air mass for several hours, returned to the operations base to refuel and exchange crew. The balloons were located again by the radio signals of location, and another sampling interval commenced. The flight patterns generally consisted of a series of circles, each lasting about 30 min. A variety of altitudes from 30 to 2500 m above sea level (asl) were flown.

The first Lagrangian experiment (A), R18-R20, December 1-2, 1995, consisted of three flights. The second (B), R23-R26, December 7-8, 1995, consisted of pre-Lagrangian characterization of the source air behind a weak frontal system, followed by the three Lagrangian flights. *Huebert et al.* [this issue] discuss the marine sulfur aerosol budgets during the ACE 1 Lagrangian experiments, and *Russell et al.* [this issue] detail mixing within the marine boundary layer. A model of the chemistry during Lagrangian B has been made by *Suhre et al.* [this issue].

2.2. Aircraft Instrumentation

A modified TECO 48 gas filter correlation analyzer was used for CO measurements on the NCAR C-130. The optics were modified as recommended by *Dickerson and Delany* [1988]. The instrument was operated in a 7 min measurement cycle, with 5 min of ambient measurement and 2 min of zeroing. The zeroing was accomplished by diverting the sampled air over a heated Pd catalyst to remove the CO

[*Parrish et al.*, 1991]. Ambient air was dried by passing it over a CaSO_4 trap before sampling. The ambient mixing ratios were reported on the basis of dry air. The signal from the analytical instrument was recorded on the central data acquisition system of the aircraft.

The instrument was calibrated every three flights with a standard cylinder of CO (0.66 ppmv) that was referenced against a National Institute of Standards and Technology (NIST) SRM and calibrated by the National Oceanic and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostics Laboratory (CMDL). The accuracy of the measurements was 15%. The instrument has considerable zero drift introduced by local temperature changes. The zero values were fit to a cubic spline, and this baseline was subtracted from the signal to obtain the analytical measurements. Aircraft vibration causes additional noise in the signal, and a series of software filters were used in the data processing to reduce this noise.

2.3. Ship Instrumentation

Measurements of atmospheric CO mixing ratios were made on the NOAA ship *Discoverer* by an automated gas chromatographic system. Sample air was continuously drawn through a sample inlet located forward of the ship's bridge. Periodically, sample air was drawn into a 3 mL sample loop and then injected into a He carrier gas stream that carried the sample through a 60/80 mesh molecular sieve 5A chromatographic column and into a hot mercuric oxide reduction detector (RGD2, Trace Analytical Inc., Menlo Park, California). The system was a simplified version of that described by *Bates et al.* [1993], the major difference being

Table 1. Intercomparison of *Discoverer* and C-130 Aircraft CO Measurements Over the South Tasman Sea

	Discoverer	C-130	C-130
Research flight number ^a /date ^b	Nov. 25, 1995	R15 Nov. 25, 1995	R15 Nov. 25, 1995
Time ^b	0030-0538	0100-0142	0400-0431
Sampling altitude (m)	7	30	30
Average CO concentrations ppbv	59.7	69.2	66.5
Standard deviation	6.0	6.9	7.4
Number of samples ^c	10	1434	1136
Research flight number ^a /date ^b	Dec. 5, 1995	R22 Dec. 5, 1995	R22 Dec. 5, 1995
Time ^b	0412-1032	0429-0459	0752-0833
Sampling altitude (m)	7	30	30
Average CO concentrations ppbv	59.5	65.6	62.7
Standard deviation	6.2	14.2	7.7
Number of samples ^c	10	1064	1556

^a See *Bates et al.* [this issue].

^b Time reference to UTC.

^c The *Discoverer* data are individual samples; the number of samples for the C-130 aircraft is the number of 1-s data points.

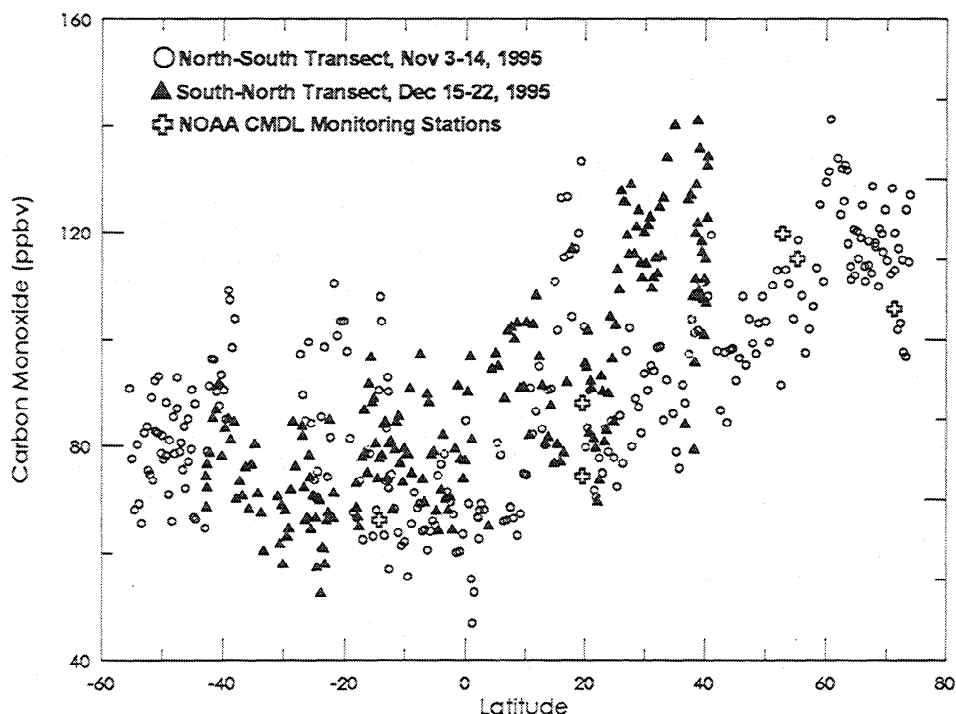


Figure 1. Airborne carbon monoxide measurements from 76°N to 59°S. The measurements were made at altitudes between 3 and 7.9 km.

the absence of the extra detectors and columns needed to measure methane and carbon dioxide. Each individual sample took 5 min to analyze, and the system operated on a 40 min cycle that included two or three ambient air measurements, two or three injections of air from a seawater equilibrator to measure the partial pressure of CO in seawater, and two or three injections of two bottled CO standards (40 and 71 ppbv) that had been calibrated against standards at NOAA CMDL. The uncertainty of the air measurements can be estimated from the sigma/mean of chromatographic peak areas of 10

identical air standards during 5 hour periods. These were typically in the range of 6 to 10%.

To reduce the noise in the calculated mixing ratios from the individual samples, the data were averaged into 6 hour periods. Periods of ship pollution were identified by continuous measurements of particle concentrations from a CN counter that had a sample inlet next to the CO sample inlet. Data during periods of ship pollution were excluded from the averaging process.

Continuous radon (Rn) measurements were also made

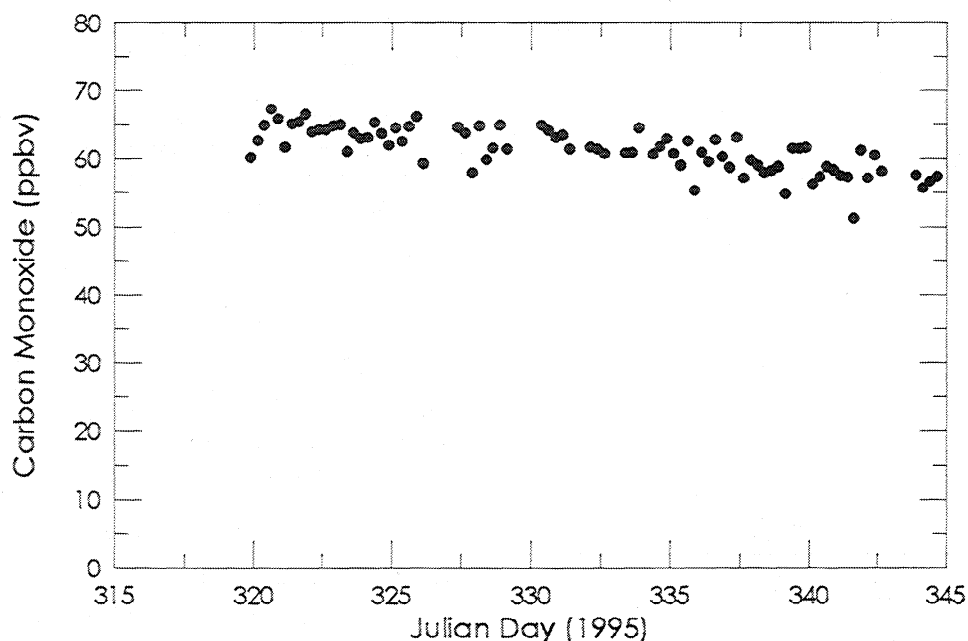


Figure 2. Six hour average CO measurements over the South Tasman Sea from the *Discoverer*.

aboard the *Discoverer*. Rn serves as one of the best tracers of continental air, when atmospheric measurements are made out over the open ocean. The criterion for background air at Cape Grim (40.75°S, 144.7°E) is a Rn level of less than 100 mBq m⁻³ [Whittlestone *et al.*, this issue]. This criterion was established for background measurements on the *Discoverer*. All CO measurements where the Rn levels were in excess of 100 mBq m⁻³ have been discarded as contaminated from continental regions.

2.4. Ship/Aircraft Measurement Intercomparison

Comparisons between the CO measurements made on the ship and on the aircraft were possible when the aircraft flew close to the ship. These comparisons were made on two separate flights (Table 1). The aircraft CO data are slightly higher than that from the ship, by an average of 14 and 8% for the two comparisons. There is no statistical difference

between the two data sets. This comparison is important as it indicates that the two data sets have no significant calibration or analytical differences.

3. Aircraft Transect Measurements

Figure 1 gives CO data from 76°N to 59°S measured on the outbound ferry between November 3 and 14, 1995 (circles), and for the period December 15–22, 1995 (triangles), on the return flight from Hobart to the Jefferson County Airport in Colorado. On the return flight, from 38°N, the flight track was over the continental United States. This figure includes all measurement data between 3 km and 7.9 km in altitude. A majority of the data, 86%, was at an altitude 5 km or greater. The data set is along a single track between 62°N and 44.5°S. At either end of the N-S transect, duplicate measurements were made on the flights to the northernmost and southernmost points. Each data point represents a 4 min measurement average.

The N-S hemispheric gradient in CO is clearly visible in Figure 1. There are two regions of elevated CO, above the general N-S hemisphere trends. Between 18° and 36°N in both of the transect flights, there are significantly elevated CO concentrations, up to about 140 ppbv. No correlations with ozone are seen in this data. A second region of elevated CO is observed in the N-S transect between 10° and 38°S. There is a strong correlation between CO and ozone concentrations in this region, and ozone concentrations up to 95 ppbv were measured at an altitude of 5500 m at 20°S.

Carbon monoxide data from five of the NOAA/CMDL cooperative air sampling network sites along the transect flight path are shown in Figure 1 by the cross symbols. The CO data from NOAA/CMDL were selected for the N-S transect only, and flask sampling times were chosen to be within 6 days on either side of the aircraft flight. The NOAA/CMDL CO data includes measurements from the following stations: Barrow, Alaska (71.32°N, 156.60°W), Cold Bay, Alaska (55.20°N, 162.72°W), Mauna Loa, Hawaii (19.53°N, 155.58°W), Cape Kumukahi, Hawaii (19.52°N, 154.82°W) and Tutuila, American Samoa (14.25°S, 170.57°W). The flight track was within 10° longitude of each of these stations. Each NOAA CO data point represents between 2 and 12 flask samples from 1 or more days. There is excellent correlation between the CO measurements from the aircraft transect and the ground stations.

From September 30 to October 11, 1994, the Measurement of Air Pollution from Satellites experiment (MAPS) measured CO over the globe from the space shuttle [Connors *et al.*, 1996]. Two regions of elevated CO were measured over the Pacific in approximately the same regions as were observed in the ACE 1 study. In the NH, the origin of the elevated CO was not clear but appeared to trace back to the industrial regions of southern Asia. The SH CO plumes could be traced back to fires in northern Australia. The MAPS experiment was about a month earlier than the ACE 1 measurements, but the increases in CO over the background were comparable.

4. South Tasman Sea Measurements

4.1. *Discoverer* CO Measurements

The seasonal change in the ambient concentration of CO is clearly seen in the entire *Discoverer* data set given in Figure 2. The *Discoverer* data are averaged into 6 hour time segments. The SH CO maximum is reached in September-

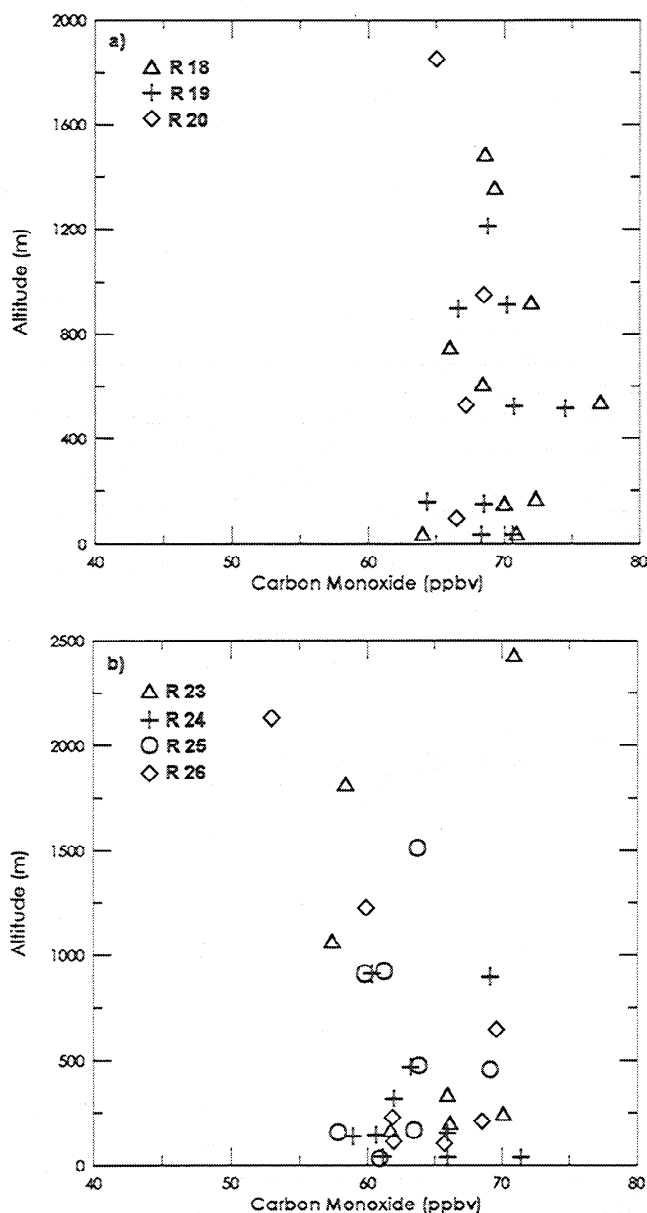


Figure 3. Details the vertical profile of CO measurements from (a) Lagrangian A, December 1–2, 1995, and (b) Lagrangian B, December 7–8, 1995.

October, and the increased concentration of OH as the SH moves into summer reduces the ambient CO concentrations [Novelli *et al.*, 1992]. Over the 25 day measurement period, the ambient CO decreased at a rate of 0.31 ppbv/d. This seasonal decrease in CO is very similar to that observed by Brunke *et al.* [1990] during the 1980s at Cape Point (34.35°S, 18.48°E) South Africa. They measured decreases of 0.27–0.40 ppbv/d in years without El Niño events.

The 845 individual CO measurements from the *Discoverer* were averaged into 1-hour bins to examine if a diurnal variation in the CO concentration was present. No evidence was found. This contrasts with the CO measurements of Thompson *et al.* [1993] in the central Pacific, which show a 1 ppbv diurnal variation in the CO concentration. Diurnal variations of CO in seawater of a factor of 5 in the Atlantic Ocean near the equator have been measured by Conrad *et al.* [1982]. This diurnal variation is driven by photo oxidation of dissolved organic matter in the ocean. On the other hand, measurements of CO over the North Atlantic during 1986 by Piotrowicz *et al.* [1990] do not show a diurnal variation in the atmospheric CO concentrations. In the ACE 1 study area, the concentration of dissolved organic matter may have been too small for this effect to be observed.

4.2. Aircraft CO Measurements

Figures 3a and 3b detail the CO vertical profile mixing ratios for the two Lagrangian experiments over the South Tasman Sea. Each data point is the average CO mixing ratio for the nominal 30 min circle at a given altitude. Since the CO instrument has a duty cycle of approximately 60%, the total measurement time is 18 min. Circles at a given altitude were repeated during some of the flights. The altitude data in Figure 3 are a corrected pressure altitude to take into account the local pressure effects.

The CO data in Figure 3a show the CO concentrations to be well mixed up to an altitude of 2000 m. This indicated long-term uniformity of the air mass, as the lifetime of CO in the atmosphere is several months. In contrast, the CO measurements for the Lagrangian B (Figure 3b) show much greater variability in CO concentrations. The overall concentrations were slightly lower for Lagrangian B and were frequently below 60 ppbv. The lowest CO concentration of 53 ppbv is measured at 2130 m on R26. The lower CO concentration coupled with elevated ozone and low water vapor concentrations suggests that this air was of stratospheric origin several days or weeks earlier. The ozone concentration at 2130 m averaged 35 ppbv, compared to 20 ppbv at lower altitudes. The increase in ozone was correlated with a drop in the water vapor mixing ratio from 3.5 g/kg at 1225 m to 1.3 g/kg at 2130 m. These concentration changes contrast to the measurements made at 1820 and 2430 m on R23. The ozone concentrations were an average of 21 and 22 ppbv, respectively, and the water vapor dropped from 5.0 to 3.1 g/kg with the increase in altitude. Comparing the CO concentrations in Lagrangian A and B, the CO concentrations for Lagrangian B were lower, and the larger variability in concentrations indicates that the air masses sampled were not as homogeneous.

5. Conclusion

The CO measurements made as part of the ACE 1 program provide a unique set of transect measurements from 76° N to 59° S and an intensive set of measurements over the South

Tasman Sea in November and December of 1995. The transect measurements clearly show the northern hemisphere-southern hemisphere gradients in CO. Elevated CO was measured in the equatorial regions. Detailed measurements of CO from the research vessel *Discoverer* did not show a diurnal pattern in the CO concentrations over the South Tasman Sea. Vertical profiles for the CO concentration obtained during Lagrangian B indicated the potential of stratospheric air mixed into the sampling region.

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